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**AN INVESTIGATION
OF
NEW LIQUID OXIDIZERS**

PREPARED FOR
OFFICE OF NAVAL RESEARCH
CONTRACT NO. NOnr-285-(28)

692-342

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Final Summary Report

for the period

February 1958

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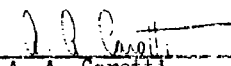
January 1, 1957 - November 30, 1957

AN INVESTIGATION OF NEW LIQUID OXIDIZERS

Prepared by
Research Division
College of Engineering
New York University
for
Office of Naval Research
Contract Nonr-285-(29)


P. F. Winternitz
Project Director

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A. A. Carotti
Associate Project Director

Report No. 488-4

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I. Preface

This report is divided into two sections, Part A and Part B. Part A is a resume of all the experimental work done from January 1, 1957 to August 23, 1957, under the supervision of Dr. Meyer M. Markowitz who left the employ of the university on August 23, 1957. Part B is the last quarterly report of the year, i.e. the work done from August 23, 1957 to November 30, 1957. This was carried out under the supervision of Mr. Arrigo Carotti who replaced Dr. Markowitz. Continuity of the work was, however, not interrupted because Dr. P. F. Winternitz directed it during the entire contract period. Also Mr. Jacobson, who performed most of the experiments and compiled the first draft of this report, worked continuously on the project.

Together, Part A and Part B constitute the work performed for the entire contract period. The main results are the following:

- A) Dilute solutions of pernitric acid have been prepared and distilled;
- B) NO_2F was synthesized by a new method;
- C) The preparation of HNO_2F_2 was attempted. No conclusive results were obtained; but there were indications for a transitory formation of a fluorinated nitrate.

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II. Summary

A. Pernitric acid, HNO_4 :

1. Attempts to prepare pure pernitric acid, HNO_4 , were unsuccessful;
2. Dilute reaction mixtures containing HNO_4 were prepared by reacting 50% H_2O_2 with 100% HNO_3 or with N_2O_3 ; but the use of 100% H_2O_2 led always to explosions;
3. The presence of pernitric acid was established from the ability of the reaction mixture to liberate bromine from its salts;
4. Pernitric acid decomposes even in dilute solutions down to a temperature of -80°C ; but the rate of decomposition decreases with decreasing temperature.
5. In spite of this instability it was possible to obtain by careful distillation a product containing more HNO_4 than the original reaction mixture. The highest concentration reached was, however, only about 7%.
6. Attempts to prepare salts of pernitric acid were unsuccessful.
7. Pernitric acid is because of its instability not useful as a practical oxidizer. For this reason, no attempts were made to improve the preparation methods developed.

B. Nitroniumfluoride, NO_2F :

1. NO_2F was prepared by the reaction of NO_2ClO_4 with NaF in nitromethane. This new method of preparation, which does not involve the use

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of elemental fluorine, is analogous to a method for the preparation of NOF developed at N.Y.U. (1) (2).

2. The identity of NO_2F thus prepared was established by chemical and physical tests.

3. The purpose of preparing NO_2F was to use it as an intermediate in the synthesis of fluoronitric acid.

C. Fluoronitric Acid, HNO_2F_2

1. Attempts to prepare HNO_2F_2 using 40% aqueous HF as the fluorinating agent under various experimental conditions were unsuccessful, probably because of the ease with which HNO_2F_2 hydrolyzes;

2. Some indications were obtained for the intermediate formation of HNO_2F_2 by the reaction of CoF_3 and NOHSO_4 in conc. sulfuric acid;

3. The reaction of KHF_2 with NO_2ClO_4 in nitromethane gave products containing both fluoride and nitrate ion. It has, however, not been established whether the initially formed NO_2F will give with anh. HF the desired fluoronitric acid or merely a complex such as $\text{NO}_2\text{F} \cdot \text{HF}$.

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III. PART (A) (Abstract of the experimental work done from Oct. 1st, 1956 to Aug. 23, 1957).

A.) Introduction

The work during the period from October 1st, 1956 to August 23rd, 1957 was concerned with two main objectives:

- 1.) The preparation and study of pernitric acid;
- 2.) The preparation and study of fluoronitric acid.

The first objective was partially fulfilled in that a new method for the preparation of pernitric was devised and some concentration by distillation was obtained. The work adds some new evidence for the existence of pernitric acid. Simultaneously it appeared, however, that there is little chance of practical application of HNO_4 as an oxidizer. For this reason the work was discontinued, but its continuation would probably be of some scientific interest.

No fluoronitric acid was actually prepared, although some indications for its formation as an intermediate were obtained. This work was continued in the remaining contract period.

The results of the work performed until the end of August were reported at the third bipropellant conference held in Sacramento, Calif., on October 15th and 16th, 1957 and a copy of the presentation was submitted to ONR, Washington, because no official minutes of the conference will be available.

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B.) Preparation of pernitric acid; (HNO₄)

a) Perhydroxylation of nitric acid.

Attempts were made to prepare HNO₄ by the following reaction (perhydroxylation):



- 1.) In the first series of experiments 100% H₂O₂ and 100% HNO₃ were reacted in various proportions. The reaction at a mole ratio 1:1 was studied at -85°C, 0°C and 20°C, both in the presence and in the absence of light. In no case was HNO₄ detected. (Anh. HNO₃, prepared per ref. (3) was used; it analyzed 101.8% by base analysis, indicating the presence of some N₂O₅.)
- 2.) The above experiments were repeated using 1:1 mole ratios of 100% HNO₃ and 50% H₂O₂; HNO₄ was obtained when the reaction was carried out at temperatures of -85°C and 0°C. The presence or absence of light had no effect. At 20°C no HNO₄ was present in the reaction mixture. Positive tests were also obtained at a mole ratio of 1:2 (100% HNO₃ to 50% H₂O₂).
- 3.) Vacuum distillation of HNO₃ - 50% H₂O₂ mixtures from -85°C to room temperature gave distillates containing HNO₄ in yields up to 5.01%.
- 4.) Attempts were made to prepare a pernitrate salt by reacting mixtures of 1 g. KNO₃, 0.65 ml. 100% HNO₃ and 0.55 ml. 100% H₂O₂ at temperatures ranging from -85°C to room temperature. HNO₄ was present in the solution. The salt was precipitated by cooling the solution to 0°C and adding glacial acetic acid.

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The solid was filtered; both the solid and the filtrate showed pernitrate content. However, it was later found that the pernitrate content of the solid was due to some adhesion of the mother liquor. Further precipitation experiments were carried out by varying the molar ratios of the constituents but no pernitrate activity was found in any of the solids isolated.

- 5.) Further attempts towards the preparation of a pernitrate salt were made using H_2O_2 , HNO_3 - nitrate salt mixtures. The nitrate salts used were $Ca(NO_3)_2$, $Al(NO_3)_3 \cdot 9H_2O$, $Sr(NO_3)_2$, $NaNO_3$, $Ba(NO_3)_2$, $Pb(NO_3)_2$, $Fe(NO_3)_3 \cdot 6H_2O$, $AgNO_3$, $Cu(NO_3)_2 \cdot 3H_2O$, NH_4NO_3 and $LiNO_3$. This method of preparation of pernitrate salts was not successful; but the moderating effect of some of the nitrate salts on the H_2O_2 - HNO_3 mixtures was quite striking.

b) Ozonization of nitric acid

The intended reaction was



- 1.) KNO_3 - O_3 : KNO_3 dissolved in H_2O and in CCl_4 was ozonized at $0^\circ C$; the salt was recovered unchanged, showing the non-occurrence of the reaction:



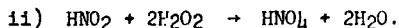
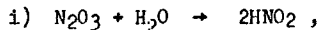
- 2.) HNO_3 - O_3 : 5 ml. 100% HNO_3 was ozonized in an ice-salt bath. No peracid was formed.
- 3.) HNO_3 , KNO_3 - O_3 : 1 g. KNO_3 in 5 ml. HNO_3 was ozonized at $0^\circ C$. Again negative results were obtained.

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c) Perhydrolyses of N_2O_5 N_2O_3

The intended method of preparation consists in reacting N_2O_5 or N_2O_3 with H_2O_2 .

- 1.) 0.17 ml. 100% H_2O_2 and 0.59 g. N_2O_5 were reacted at $-85^\circ C$; an immediate explosion occurred without the formation of HNO_4 . This experiment was repeated with similar results (4).
- 2.) 0.92 g. N_2O_5 was vacuum distilled onto 0.29 ml. 100% H_2O_2 at $-85^\circ C$; upon warming an explosion occurred. This experiment was repeated, again an explosion took place but this time HNO_4 was present in the residual liquid.
- 3.) 0.13 ml. of H_2O_2 was vacuum distilled onto 0.51 g. N_2O_5 at $-85^\circ C$; upon warming an explosion occurred with no indication of the presence of HNO_4 .
- 4.) 0.4 g. of N_2O_3 was reacted with 0.66 ml. 50% H_2O_2 in an ice-salt bath. The resulting solution contained HNO_4 . This was thought to occur as follows:



The experiment was repeated using 0.87 g. N_2O_3 and 0.87 ml. 50% H_2O_2 . A 6.54% yield of HNO_4 was realized.

d) Miscellaneous attempts to prepare HNO_4

- 1.) Reactions of H_2O_2 with salts. 1 g. KNO_3 was refluxed with 5 ml. 50% H_2O_2 for 5 hours; no evidence of pernitrate activity was found. 1 g. $NaNO_2$ and 5 ml. 50% H_2O_2 were refluxed for 3 hours; again no evidence for pernitrate activity was found.

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- 2.) 2 g. Na_2O_2 were reacted with 10 ml. 70% HNO_3 (in excess). This reaction resulted in the formation of pure NaNO_3 rather than NaNO_2 .
- 3.) The reaction of KHSO_5 and HNO_3 did not produce any HNO_2 .
- 4.) The reaction of $\text{K}_2\text{S}_2\text{O}_8$, H_2O , H_3PO_4 , and HNO_3 did not produce any HNO_2 .

C.) Attempted Preparation of a Fluorinated Nitric Acid

a) Simultaneous Oxidation and Fluorination

In one set of experiments nitrous acid was prepared by hydrolysis of nitrosyl-sulfuric acid and then reacted with cobaltic fluoride to obtain simultaneously oxidation of the nitrogen and reduction of the cobalt ion.

- 1) 4.1 g. CoF_3 were added to 50 ml. 95.8% H_2SO_4 and 2.3 g. NOHSO_4 . The mixture was refluxed for 2 hours at 100°C and then vacuum distilled at 100°C . It was hoped to prepare HNO_2F_2 as follows:

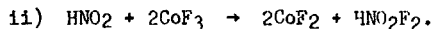
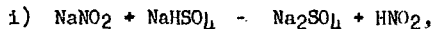


Analyses of the distillate showed it to contain H_2SO_4 , H_2SiF_6 , and probably some HF and HNO_3 either as such or stemming from the hydrolyses of HNO_2F_2 during the course of the analyses. The experiment was repeated, the mixture was refluxed at 190°C for 2 hours and vacuum distilled at 100°C . Similar results were obtained. The experiment was repeated again with refluxing at 180°C for 2 hours and vacuum distilling to 180°C ; again similar results were obtained. In the above three cases HNO_3 was found

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in the distillate. It is significant that when the CoF_3 reactant is not placed in the above mixtures then no HNO_3 is found in the distillate: it appears that CoF_3 may have reacted with the small HNO_2 present to yield a material separable by vacuum distillation from the bulk of the reaction medium.

- 2) A dry reaction mixture of 2.2 g. NaNO_2 , 5.6 g. NaHSO_4 and 7.6 g. CoF_3 was vacuum distilled while being heated from 24°C to 150°C over a period of three hours. The distillate was similar to that found in the previous experiments. The attempted reaction scheme is:



b) Exchange Reactions

Exchange reactions involving various fluorine compounds and nitric acid or resp. nitrates were also studied.

- 1) Mixtures of HNO_3 and FSO_2OH were refluxed for extended periods at 100°C and 165°C , followed by vacuum distillation. In no case did the distillates contain HNO_3 indicating no conversion as per the equation:



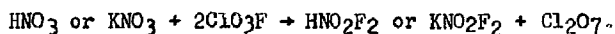
A mixture of HNO_3 , FSO_2OH and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (which decomposes under reaction conditions to yield $(\text{NaPO}_3)_n$ and H_2O) was refluxed at 100°C and 165°C and then vacuum distilled; no nitrate was obtained in the distillate.

- 2) Distillates obtained from mixtures of HNO_3 and $\text{H}_2\text{PO}_3\text{F}$ after refluxing and vacuum distillation contained less than 1% F indicating that no HNO_2F_2 was formed.

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3) HF (40% aqueous solution) was reacted with KNO_3 in polyethylene and platinum containers, followed by evaporation to dryness. Analyses of the reaction mixture showed essentially pure KNO_3 (92.3%, 99.1%) along with some conversion of the salt to KF. Apparently no HNO_2F_2 was formed.

4) ClO_3F was reacted with KNO_3 and HNO_3 in attempts to promote the reaction:



After passage of ClO_3F through HNO_3 and mixtures of KNO_3 and HNO_3 at 0°C , no F was found in the mixture confirming the absence of a reaction.

5) A reaction mixture of CoF_3 and HNO_3 in 96% H_2SO_4 was refluxed at 100°C for 3 hours and then vacuum distilled. Analyses of the distillate showed it to contain 76.5% HNO_3 , 6.1% H_2SiF_6 , 5.4% HF and 12% H_2O (by difference). The small fluoride content would indicate but negligible attack of the nitric acid by the cobalt trifluoride.

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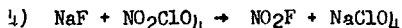
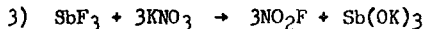
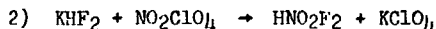
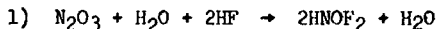
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IV. Detailed report on work performed from August 23rd to November 30th, 1957.

A.) Introduction

During the report period emphasis was placed on the preparation of nitroniumfluoride and of fluorinated nitric acid. These attempts appeared to be attractive because a four coordinated nitrogen atom with a positive charge is capable of existing and it would seem from theoretical considerations that this is the state required for these compounds (5)(6).

The following methods were used in our attempts to prepare them:



They are described in some detail in the next section. The first two of them are concerned with fluoronitric acid, the last two with nitroniumfluoride. Since conventional laboratory set-ups were used no detailed description appears to be necessary.

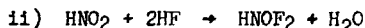
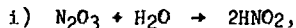
B.) Experimental

- 1.) Attempts to prepare fluoronitric acid from N_2O_3
and 40% aqueous hydrofluoric acid.

Mixtures of 40% aqueous HF and excess N_2O_3 were reacted at -85°C and allowed to warm up gradually to room temperature.

The scheme of the reaction is:

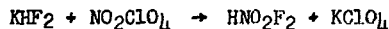
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The occurrence of a reaction could be visually observed; however, analysis of the products showed them to be a mixture of 2-1/2 moles HF and 1 mole HNO₃ diluted in 5 moles H₂O, which correspond to the original reactants. The N₂O₃ was made by reacting concentrated HNO₃ with NaNO₂ in a gas generator and collecting the N₂O₃ formed in a receiver kept at -85°C (7).

- 2.) Attempts to prepare fluoronitric acid from nitroniumperchlorate and KHF₂.

The intended reaction was:



In one experiment an excess of KHF₂ was reacted with 2 gms NO₂ClO₄ dissolved in nitromethane for two hours at room temperature (16°C), 2 hours at 20°C, 2 hours at 40°C, and 2 hours at 60°C. Nitrogen was continuously passed through the reaction mixture and vapors formed by the reaction were absorbed at 0°C in a trap containing sodium hydroxide. The sodium hydroxide turned an amber color during the reaction. Analyses of the NaOH gave a positive brown ring nitrate test (8) and a positive fluoride test (alizarin red S and Zr(NO₃)₂ (9)). A positive fluoride test was also obtained with CaCl₂. 5 ml. of the NaOH solution was used for quantitative determination of nitrate by the Nitron procedure but no precipitation occurred (See Appendix "Analytical").

This reaction was then repeated using about 4 g. NO₂ClO₄ and an excess of KHF₂; three traps were placed in the apparatus,

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the first one was kept at room temperature (20°C), the second one at -50°C and the third one at liquid nitrogen temperature (-196°C). The temperature was raised gradually from 20°C to 80°C during a period of 4 hours. 5-6 ml. of liquid was collected in the trap I, a brownish solid in trap II, and a white solid in trap III. The liquid in trap I was not miscible with H_2O , but proved to be acid to litmus paper. Analyses of the liquid showed both fluoride and nitrate ion to be present.

The nitroniumperchlorate used in these two attempts had been prepared by the following method (10): A solution of N_2O_5 (excess) in nitromethane at -20°C was added to a solution of anhydrous HClO_4 in nitromethane at -20°C . NO_2ClO_4 precipitated out and was filtered on a sintered glass funnel and then dried under reduced pressure in a dessicator. This work was done in a dry nitrogen box to prevent hydrolyses of both the reactants and the products. The anhydrous HClO_4 used had been prepared by vacuum distilling a mixture of 640 ml. 96% H_2SO_4 and 160 ml. 72% HClO_4 and the N_2O_5 was prepared by adding P_2O_5 to frozen white fuming HNO_3 and ozonizing the resultant vapors given off on warming of the mixture (11). Base analyses of the nitronium perchlorate showed it to be 100.5% NO_2ClO_4 , traces of N_2O_5 causing the deviation from 100%.

For a third attempt NO_2ClO_4 was prepared by a different method. 3 ml. of 72% HClO_4 was added to 5 ml. of nitromethane at -20°C ; then 30 g. N_2O_5 was dissolved in 40 ml. of nitromethane at the same temperature and the two solutions were mixed; a white

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precipitate formed and was filtered off. About 3 g. NO_2ClO_4 thus prepared were reacted with an excess of KHF_2 , for a total of 6 hours; (2 hours at 40°C , 2 hours at 60°C and 2 hours at 80°C) in the same apparatus as used in the previous experiment. The contents of the three traps were analyzed qualitatively for fluoride and nitrate ion, the results being tabulated below. Trap I contained about 1 ml. of a clear liquid, Trap II contained a brownish solid at -50°C , and Trap III contained a white solid at -196°C . The liquid in Trap I was not miscible in about 2 ml. of water but did dissolve on addition of more water. Trap II was allowed to warm to room temperature and its volatile content was passed in a nitrogen stream over a period of two hours through a solution of NaOH in water. A colorless liquid and a small amount of a white solid remained after the nitrogen scrubbing. The following morning the white solid had disappeared and the trap was filled with a brown vapor. The NaOH solution was analyzed and is labeled Trap IIb in the table below. NaOH was added to Trap III and allowed to warm up to room temperature; upon addition of the NaOH a blue color was observed which did, however, disappear upon warming to room temperature.

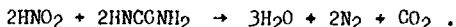
Table I

Test	Trap I	Trap II	Trap IIb	Trap III
F^-	Pos	Pos	Pos	Pos
NO_3^-	Pos	Pos	Pos	Pos
NO_2^-	-	Pos	Pos	Neg

The nitrite test was performed by cooling a solution of urea and the sample to 0°C and acidifying, an evolution of bubbles

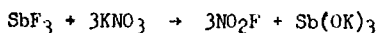
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indicating the presence of HNO_2 (12) according to the equation:



- 3.) Attempted preparation of nitroniumfluoride from antimony trifluoride and potassiumnitrate.

The intended reaction is represented by the equation:



Four experiments were performed.

In the first experiment a dry mixture of 1.7 g. KNO_3 and 1 g. SbF_3 (13) was reacted at various temperatures in stainless steel equipment. At 55°C no observable reaction took place and no distillate appeared in the receiver, held at -85°C . At 100°C again no distillate was observed after 2-1/2 hours, but acid fumes were noted when the apparatus was flushed with nitrogen. At 125°C a few particles of a white solid at -85°C were noted which, when dissolved in water, gave a positive nitrate test and a negative quantitative fluoride test. At 145°C at the bottom of the receiver, a solid white product collected which melted and vaporized below room temperature to give a colorless gas. The water solution had a pH of 5; analyses of the solution gave a negative quantitative fluoride test.

The second reaction was carried out in glass apparatus at temperatures from 150°C - 170°C . Brown vapors escaped and after 5 hours a mixture of a brownish solid and a light blue solid had accumulated in the receiver which was kept at liquid nitrogen temperature. On warming to -35°C , a solid evaporated almost

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completely; the remaining solid released brown vapors. The relative amounts of nitrate and fluoride present in the reaction mixture at the start and at the end of the experiment are tabulated below.

Table II

	Start	After reaction	Lost
% KNO_3	38.26	26.25	12.01
% SbF_3	12.10	6.73	5.37

The above analyses correspond to the removal of an empirical compound $(\text{NO}_2)_2\text{F}$ or an equimolecular mixture of NO_2 and NO_2F from the reaction mixture. A very small part of the reaction mixture turned a blue-green color; it was excised and analyzed for fluoride, 11.42% fluoride was found as compared to the initial content of 12.10%.

In the third reaction a light blue solid product was collected in the trap at -196°C . It reacted with water. The resulting solution contained 5.5 mg. nitrate and no fluoride.

In the fourth attempt three traps were placed in the apparatus; the first trap contained 13 g. NaOH at 0°C , the second trap contained water at 0°C and the third trap was kept at -196°C . Dry nitrogen was passed through the apparatus throughout the entire experiment.

The weight of the NaOH increased by 0.2 gms. It contained 39.8% nitrate and no fluoride.

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4.) Preparation of NO₂F from NaF and NO₂ClO₄

The intended reaction was:



Three experiments were performed.

In the first test an excess of NaF (3.4 g.) was mixed with 1.5 g. NO₂ClO₄ in anhydrous nitromethane and reacted for 6 hours at 50°C; a white solid was collected in the receiver at -196°C. The receiver was allowed to warm up, however, because of the small amount of product available its boiling point was not observable. 19 ml. of gas were collected in a mercury gas burette and passed into an evacuated flask containing frozen NaOH, which after warming up was titrated with standard acid. The gas was found to have reacted with 0.001 moles of base, approximately in a 1:1 mole ratio. The NaOH solution contained after absorption of the gas nitrate (brown ring test) and fluoride (alizarin red S and Zr(NO₃)₂ solution).

In the second reaction larger quantities, namely, 6.4 gms NO₂ClO₄ and 5.9 gms of NaF were used. After 4 hours the receiver was connected to a flask containing a known amount of frozen NaOH. Upon warming the solid product vaporized and passed through the attached mercury bubbler, reacting with the mercury. The NaOH was back titrated and a smaller quantity of base was found to have reacted than in the previous experiment. Qualitative analyses showed the NaOH not to contain any fluoride. The reaction was then continued and the gases evolved bubbled through NaOH. This NaOH solution turned a yellow green color and gave a positive test for both fluoride and nitrate.

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The reaction was run again using ca. 8 g. NO_2ClO_4 ; a liquid slurry was collected in a trap kept at -132°C (frozen pentane) indicating the melting point of the product; a boiling point was observed in the temperature range -70°C to -65°C . An approximate yield based upon a density of 2.9 g./ml. is 60-80%.

C.) Discussion

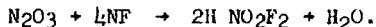
The product of the reaction between sodium fluoride and nitroniumperchlorate (reaction 4 in the experimental section) had a B.P. of -70°C to -65°C and a F.P. of -135°C to -132°C . It gave a positive test for fluoride and nitrate and turned moist blue litmus paper red. It reacted with H_2O , NaOH , Hg and Tygon and fumed in air. According to these properties it was NO_2F .

On the other hand no NO_2F resulted from the reaction of KHF_2 and NO_2ClO_4 (reaction 2 in the experimental section). But all products contained fluoride and nitrate. The product collected at -50°C (trap II) evolved some NO_2 after nitrogen scrubbing, leaving a white solid residue which disappeared on standing overnight at room temperature. The formation of an unstable compound such as the intended fluoronitric acid would be compatible with these observations. But an addition compound $\text{NO}_2\text{F} \cdot \text{HF}$ might behave in the same way. Further study would be required to decide between the various possibilities.

The analysis of the products of the reaction of N_2O_3 and 40% aq. HF corresponded to a mixture of 2-1/2 moles HF and 1 mole HNO_3 diluted in 5 moles H_2O . The presence of water in the hydrofluoric acid used is, of course, quite detrimental to the intended formation of

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HNO_2F_2 because one would expect this compound to be readily hydrolyzed. But even anhydrous hydrofluoric acid would be not much better because some water is formed by the reaction itself as shown by the overall equation:



It might be possible to tie down the water of reaction by using an excess of N_2O_3 although even this is somewhat questionable. In experiments carried out by us with excess N_2O_3 the latter boiled away before the reaction started. But performing the reaction in a bomb might give more favorable results.

In the reaction of antimony trifluoride with potassium nitrate, (reaction 3 of the experimental section), the product collected contained no fluoride. However, in many cases the glass reaction vessel was very badly etched, indicating the presence of fluorides. The loss of nitrate and fluoride from the reaction mixture corresponded roughly to a compound containing FNO_2 and NO_2 in the mole-ratio 1:1; apparently some of the fluorine compounds had reacted with the glass. At this point it cannot be stated whether the observed mole ratio of NO_2 to FNO_2 has any significance. Various shades of blueish and greenish colors were observed in the reaction mixture. But they disappeared on exposure to the air. The possible formation of the compound K_3Sb is indicated by these observations which would of course presuppose a reaction of SbF_3 and KNO_3 . Termination of the contract work prevented further study of these reactions.

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D.) Conclusions

From the experiments described and from their discussion the following can be concluded:

1. The reaction of sodium fluoride and nitronium perchlorate, produces nitronium-fluoride. Other volatile nitronium-compounds can most probably be prepared in a similar way.
2. The reaction of potassium acid fluoride and nitronium perchlorate does proceed in a different way. No nitronium-fluoride is formed. The products however, contain in all cases fluoride and nitrate ions indicating that a reaction had taken place.
3. No positive results were obtained for the formation of fluorinated nitric acid in the reaction of N_2O_3 and 40% aqueous HF at $-85^\circ C$.
4. The reaction between antimony trifluoride and potassium nitrate produced volatile products, the nature of which could not be ascertained within the period of time available.

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V. Recommendations for future work:

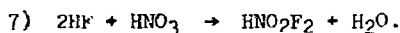
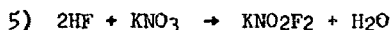
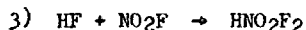
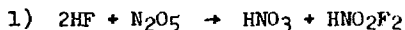
The following recommendations are made:

a) The reaction between NaF and NO_2ClO_4 to produce FNO_2 should be investigated further as to the use of fluorides (14) other than NaF.

b) Analogous reactions using compounds of the type KBrF_4 , BrF_2SbF_6 and the halogen fluorides together with nitroniumperchlorate should be studied (15).

c) The reaction between KHF_2 and NO_2ClO_4 should be investigated further as to the feasibility of preparing HNO_2F_2 by this method. The use of other acid fluorides in place of KHF_2 should also be studied.

d) Methods for the preparation of a fluorinated nitric acid by reactions involving the use of anhydrous HF should be investigated in open and closed systems. Some suggestions are as follows:



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Appendix A: Analytical methods used.

A) HNO₃; Nitrate Salts:

Analyses for nitric acid content were carried out in two ways 1) base titration and 2) the use of 1,4-diphenyl-3,5-endo-anilodihydro-triazole ("Nitron" Reagent) as a gravimetric reagent for the determination of nitrates (16). The procedure used is that detailed in Treadwell-Hall (17). A check on this method was made to verify the precipitate obtained with nitron from the experimental mixtures; a gasometric procedure was chosen (18)(19). By this method the nitrate is converted to NO as per: $\text{NaNO}_3 + 3 \text{FeCl}_2 + 4\text{HCl} \rightarrow \text{NaCl} + 3 \text{FeCl}_3 + 2 \text{H}_2\text{O} + \text{NO}$. Nitron itself was found to evolve no gas during the analysis; nitron nitrate unfortunately did not evolve the theoretical quantity of NO. However the fact that NO was given off could readily be determined by passage of O₂ into the collected gas to effect the reaction. $2 \text{NO} + \text{O}_2 \rightarrow 2 \text{N}_2\text{O}$ (brown). Satisfactory results were obtained by standardization with KNO₃ and the liberation of its theoretical NO content. The nitron nitrate precipitate was substantiated by the qualitative determination of NO as collected.

B) HNO₄; peracid:

Analyses of the peracid content of the reaction mixtures used in an attempt to prepare HNO₄, were performed by first liberation of bromine as per: $\text{Peracid} + 2 \text{HBr} \rightarrow \text{H}_2\text{O} + \text{Br}_2$, followed by titration with standard sodium arsenite solution (KBrO₃ was used as the primary standard) (20)(21). Thus, $2\text{Br}_2 + \text{As}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{As}_2\text{O}_5 + 4\text{Br}^- + 4\text{H}^+$.

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C) O₃; Ozone:

In ozonization experiments with a known rate of oxygen flow (100 ml/min.), the yield of O₃ obtained was determined by passage of the effluent gas through KI solution and titration of the liberated I₂ with sodium arsenite (22).

D) SO₄; Sulfate:

The sulfate was determined gravimetrically by precipitating as BaSO₄ (23).

E) Co; Cobalt:

In the reactions using CoF₃, the quantity of Co was determined quantitatively by use of a gravimetric method (24) using alpha-Nitroso beta-Napthol as the precipitating reagent.

F) F; Fluoride:

Fluoride was analyzed by quantitatively precipitating lead fluorochloride (25). Presence of fluoride was determined qualitatively by use of the Alizarin Zirconium Lake Test (26).

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